Removing sulfur from gold using ultraviolet/ozone cleaning

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I. INTRODUCTION

Irradiating surfaces with ultraviolet (UV) light has been demonstrated to be an effective means of eliminating surface contamination from a variety of substrates. The mechanism of this UV cleaning procedure involves UV excitation of surface species and conversion of molecular oxygen to ozone and atomic oxygen. These strong oxidizers then decompose UV excited organic surface contaminants to volatile groups such as CO, CO\(_2\), N\(_2\), etc. that can desorb, and inorganics are converted to highly oxidized states that can be readily removed by rinsing with ultrapure water.

While solvent cleaning protocols are effective in some applications, contaminants are often only partially removed, and impurities present in the cleaning solvents can be introduced. The UV/ozone method is primarily a dry process that cleans substrates more rigorously than solvent methods and only requires ultrapure water for removing certain inorganics. Thus, the use of excess and often caustic solvents is avoided, and the possibility of contamination from impurities introduced by these solvents is eliminated as well. UV/ozone cleaning also contains advantages over the conventional dry method of ion plasma cleaning. Sample ion bombardment in plasma cleaning can induce surface roughening at the atomic scale. However, the UV/ozone process only affects adsorbed surface species and leaves an inert substrate such as gold intact. This is advantageous for scanning microscopy studies where atomically flat surfaces are often needed.

Although numerous studies have examined the effectiveness of the UV/ozone method in cleaning semiconductors such as silicon, relatively few have investigated UV/ozone treating metal surfaces, and these studies only concern the elimination of hydrocarbons. In recent years the self-assembly of sulfur-containing molecules via strong sulfur–gold bonding such as alkanethiols on gold has become a topic of considerable interest, and characterizing the sulfur from such thiol monolayers is often beneficial in understanding monolayer properties. Because sulfur readily adheres to gold, however, freshly deposited gold samples exposed to ambient conditions are easily contaminated with any sulfur compounds present in the laboratory air. Attempts by the authors to remove such sulfur contaminants with solvents including nitric acid and piranha solution were unsuccessful.

Gold bound alkylthiolates irradiated with UV light have been shown to convert to alkylsulfonates. Recently, this idea has been utilized to photopattern self-assembled (SA) alkanethiol monolayers on gold in which spatially patterned sulfonates formed from thiolate UV exposure are rinsed from the gold substrate with water. In the current report a similar idea is presented in which the UV/ozone cleaning protocol is demonstrated to be an effective method for eliminating sulfur impurities from gold exposed to ambient conditions as well as for removing old SA thiol monolayers to generate a fresh gold surface for future SA experiments. Experimental conditions for optimizing sulfur removal are also discussed.

II. EXPERIMENT

To examine the effectiveness of the UV/ozone cleaning procedure, cystamine (\(\text{NH}_2\text{CH}_2\text{CH}_2\text{S–SCH}_2\text{CH}_2\text{NH}_2\)) was SA on gold, and x-ray photoelectron spectroscopy (XPS) was used to characterize the surface before and after UV exposure. Cystamine was chosen because it readily forms a monolayer on gold and provides a sulfur signal that can easily be detected with XPS. All gold substrates were prepared by thermal evaporation on glass microscope slides. Prior to depositing gold, the slides were washed with soap and distilled, de-ionized (Nanopure II) water and immersed in piranha solution (30% H\(_2\)O\(_2\) and concentrated H\(_2\)SO\(_4\), 1:4 by volume) for 20 min. Caution: Piranha solution is extremely corrosive and can react violently with organic compounds. Finally, the slides were thoroughly rinsed with Nanopure water and oven dried. To provide better gold adhesion, \(\sim 10\) nm of chromium were initially evaporation deposited. Approximately 150 nm of Au were then deposited over the Cr layer at an evaporation pressure of \(\sim 2.5\times10^{-4}\) Pa.

After depositing the gold, a slide was immersed in a 10 mg/ml Nanopure water solution of cystamine (Sigma Chemical) for 18 h. The slide was rinsed thoroughly with Nanopure water after self-assembly to remove any physisorbed molecules, dried with Ar gas, and analyzed with XPS. XPS data were acquired with a Physical Electronics Industries model 5400 spectrometer using a Mg \(K\alpha\) x-ray anode at 15 kV and 400 W. Binding energy windows for the S 2\(s\), C 1\(s\), and Au 4\(f\) signals were acquired at a pass energy of 35 eV using a resistive anode encoder detection system. All spectra were obtained at a take-off angle (between the sample surface and the spectrometer) of 45°. Sample relative atomic concentrations were calculated based on empirically derived sensitivity factors.

Following XPS analysis the cystamine sample was inserted in an UV cleaner (Boekel Industries) and exposed to UV radiation for 5 min while oxygen was continuously flushed through the UV chamber. Caution: This procedure should be performed under a hood since ozone is liberated and is toxic. A low pressure quartz mercury lamp with line emissions at 185 and 254 nm was used to generate UV radiation. The sample was examined with XPS following UV/ozone treatment utilizing the same analysis times and binding energy windows as those used previously. Finally, the
A gold sample contaminated with sulfur during a week of exposure to ambient conditions was also examined with XPS before and after UV/ozone cleaning. As with the cystamine sample, the gold was UV cleaned in oxygen for 5 min and rinsed with Nanopure water. The effect of oxygen on UV cleaning was also investigated. SA cystamine on gold was UV/ozone cleaned 5 min under ambient conditions and compared with cleaning in oxygen. Prior to UV treatment in oxygen, the UV chamber was purged for 1 min with oxygen, and oxygen was continuously flushed through the system during irradiation.

### III. RESULTS AND DISCUSSION

An XPS S 2p band at a binding energy of approximately 162 eV was observed from the intact SA cystamine monolayer [Fig. 1(a)]; this is indicative of a gold bound thiolate species.\(^\text{10}\) Presumably, the cystamine disulfide bond dissociates upon chemisorbing to gold.\(^\text{11}\) A small peak located at 168 eV was also detected, characteristic of a sulfonate.\(^\text{5}\) After 5 min of UV/ozone treatment, the thiolate was converted to the 168 eV sulfonate species [Fig. 1(b)]. The ratios of the S 2p peak areas to the Au 4f areas were determined for both the thiolate and sulfonate species (Table I). While the thiolate was almost entirely transformed to the sulfonate following UV exposure, the sums of the thiolate and sulfonate peak areas were essentially identical before and after UV irradiation, indicating that no sulfur was removed by the UV/ozone process. After thoroughly rinsing the substrate with Nanopure water, though, the sulfonate peak was greatly diminished in intensity [Fig. 1(c)], presumably because the sulfonate–gold bond is much weaker than a thiolate–gold bond, and sulfonates are water soluble.\(^\text{7}\)

A small amount of SA cystamine 162 eV thiolate species was not removed following UV irradiation and rinsing with water [Fig. 1(c)]. The ratio of the S 2p thiolate peak area to the gold 4f area, however, is five times greater prior to UV exposure compared to that after UV cleaning and rinsing with water (Table I). UV/ozone cleaning followed by rinsing with water thus substantially reduces the amount of 162 eV chemisorbed sulfur present. A trace amount of 168 eV sulfonate was also detected after UV exposure and rinsing with water [Fig. 1(c)]. Since the binding energy of the sulfonate peak is shifted considerably from the thiolate peak though, any residual sulfonates should not interfere with thiolate peak analysis.

In addition to its efficacy in eliminating sulfur from a SA thiol monolayer, UV cleaning can also remove trace sulfur impurities from gold exposed to contaminated air. A 162 eV thiolate peak observed on a gold substrate left in ambient conditions [Fig. 2(a)] was no longer detected after UV clean-

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**Table I.** Ratio of the XPS S 2p thiolate and sulfonate peak areas to the Au 4f area before and after UV/ozone treating SA cystamine on gold.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thiolate</th>
<th>Sulfonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA cystamine before UV cleaning</td>
<td>0.086</td>
<td>0.013</td>
</tr>
<tr>
<td>SA cystamine after UV exposure</td>
<td>0.004</td>
<td>0.098</td>
</tr>
<tr>
<td>SA cystamine UV cleaned and rinsed with water</td>
<td>0.017</td>
<td>0.023</td>
</tr>
</tbody>
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Fig. 1. XPS S 2p window of (a) cystamine SA on gold, (b) SA cystamine UV/ozone treated in oxygen for 5 min, and (c) after rinsing with ultrapure water.

Fig. 2. XPS S 2p window of (a) gold contaminated with sulfur from ambient exposure and (b) after UV/ozone cleaning for 5 min in oxygen and rinsing with ultrapure water.
The SA cystamine control was shown in Fig. 3a. The thiolate peak of SA cystamine UV/ozone treated in ambient conditions 5 min and rinsed with ultrapure water [Fig. 3(b)]. Freshly deposited gold substrates are hydrophilic, but after exposure to air for several minutes, they become hydrophobic due to the adsorption of adventitious hydrocarbons. UV cleaning for 5 min, however, produces a completely hydrophilic surface, presumably due to the removal of hydrocarbons. No evidence of gold oxidation is observed after UV treatment, as only one Au 4f peak is detected by XPS at 84.0 eV which is the binding energy of sputter-cleaned gold.

Therefore, the gold hydrophilicity is not believed to be the result of gold oxidation. Some recontamination by adventitious carbon will occur before UV treated hydrophilic gold can be transferred to the XPS chamber for analysis. Thus, a 285 eV hydrocarbon peak is always observed after UV cleaning. UV cleaned hydrophilic gold that is immediately immersed in a solution for SA, though, should provide a surface more favorable to molecular self-assembly than hydrophobic gold which will be coated with a thicker layer of adsorbed hydrocarbons.

The effect of oxygen on removing SA cystamine sulfur from gold with the UV/ozone method was examined and is presented in Fig. 3. [The SA cystamine control was shown in Fig. 1(a).] A small thiolate peak was observed for a SA cystamine sample UV/ozone treated for 5 min in ambient conditions and rinsed with water [Fig. 3(a)]. The thiolate peak of SA cystamine exposed to the UV/ozone process in pure oxygen for 5 min [Fig. 3(b)] was not detected, however, presumably because more cystamine thiolate sulfurs were converted to sulfonates when oxygen was used. Therefore, gold should be UV/ozone cleaned under an oxygen atmosphere if maximum removal of thiolate sulfur is imperative. (Note: Oxygen was continuously flushed through the UV chamber during UV exposure. One study indicates that air flowing rapidly over a glass surface reduced the UV/ozone cleaning efficiency, possibly because UV generated ozone was swept away by the air stream. Thus, the oxygen flow rate should not exceed that necessary to provide a pure oxygen atmosphere during the UV experiment.)

Several qualitative observations were made on the relationship between UV/ozone cleaning and UV exposure time. Contact angle measurements were made versus UV treatment time of ambient exposed hydrophobic gold (Table II). While gold exposed to UV light for 2 min was considerably more hydrophilic than that prior to UV irradiation, the surface was not completely wettable, as evidenced by a contact angle of 13°. As discussed previously, however, 5 min of UV exposure resulted in a completely hydrophilic surface. Also, the SA cystamine thiolate S 2p peak area after 10 min of UV cleaning in air was essentially identical to that after a 5 min cleaning. After UV/ozone treatment in oxygen for 10 min, a subtle reduction in peak area was observed compared to that with a 5 min cleaning. Five minutes appears sufficient, though, for routinely cleaning gold prior to film self-assembly.

### IV. CONCLUSIONS

A gold surface exposed to UV light can be purged of sulfur impurities via oxidation of chemisorbed sulfur to sulfonates which can then be removed by washing with high-purity water. The UV cleaning process involves UV conversion of oxygen to ozone and atomic oxygen which then transform surface species to either volatile states that desorb, or highly oxidized molecules which are water soluble. The UV/ozone method allows one to remove old SA thiol monolayers and to provide a fresh surface for additional SA experiments. In addition, gold which has been contaminated by ambient sulfur can be cleaned by the UV protocol. Because the method only requires a UV lamp and high purity water for eliminating certain inorganics such as sulfur, the use of other chemicals required in solvent cleaning protocols is unnecessary. UV treatment is noninvasive because it only affects adsorbed surface molecules and not inert substrates such as gold. Thus surface roughening at the atomic scale which occurs with ion bombardment methods is avoided. The UV process, then, should be ideal for cleansing atomically flat gold substrates needed in scanning microscopy studies of SA monolayers.

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